

Perspectives of the disproportionation driven superconductivity in strongly correlated 3d compounds

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Abstract. Disproportionation in 3d compounds can give rise to an unconventional electron-hole Bose liquid with a very rich phase diagram from a Bose metal, charge ordering insulator to an inhomogeneous Bose superfluid. Optimal conditions for the disproportionation driven high- T_c superconductivity are shown to realize only for several Jahn-Teller d^n configurations that permit the formation of well defined local composite bosons. These are the high-spin d^4 , low-spin d^7 , and d^9 configurations given the octahedral crystal field, and the d^1 , high-spin d^6 configurations given the tetrahedral crystal field. The disproportionation reaction has a peculiar "anti-Jahn-Teller" character lifting the bare orbital degeneracy. Superconductivity in the d^4 and d^6 systems at variance with d^1 , d^7 , and d^9 systems implies an unavoidable coexistence of the spin-triplet composite bosons and a magnetic lattice. We argue that unconventional high- T_c superconductivity observed in quasi-2D cuprates with tetragonally distorted CuO_6 octahedra and iron-based layered pnictides/chalcogenides with tetrahedrally coordinated Fe^{2+} ions can be a key argument supporting the disproportionation scenario is at work in these compounds.

PACS numbers: 71.28.+d, 74.20.Mn, 74.70.Xa, 74.72.-h

1. Introduction

The origin of high- T_c superconductivity [1] is presently still a matter of great controversy. Copper oxides start out life as insulators in contrast with BCS superconductors being conventional metals. Unconventional behavior of these materials under charge doping, in particular, a remarkable interplay of charge, lattice, orbital, and spin degrees of freedom, strongly differs from that of ordinary metals and merely resembles that of a doped semiconductor. Novel non-copper based layered high- T_c materials such as iron oxyarsenide LaOFeAs [2] reveal normal and superconducting state properties very different from that of standard electron-phonon coupled "conventional" superconductors.

We believe that unconventional behavior of high- T_c superconductors can be consistently explained in frames of a so called dielectric scenario [3, 4, 5] that implies an instability of the respective parent compound with regard to d - d charge transfer (CT) fluctuations with formation of local composite bosons. This implies realisation of the Ogg-Schafroth's real-space pairing model for the Bose-Einstein superconducting condensation [6, 7]. At first sight the d - d disproportionation

$$3d^n + 3d^n \rightarrow 3d^{n+1} + 3d^{n-1} \quad (1)$$

whose energy is usually estimated to be U (U_{dd}), mean intra-atomic electron-electron (Mott-Hubbard) repulsion energy, is rather uncommon and a priori much more expensive in narrow-band 3d transition-metal compounds as compared with compounds containing broad-band $6s^1$ ions such as Bi^{4+} , Pb^{3+} or Tl^{2+} due to their strong tendency to form $6s^0$ and $6s^2$ closed shells [8]. Experimental values of the minimal energies of the d - d CT, or Mott-Hubbard transitions in different 3d oxides as usually derived from the optical gap measurements, $\Delta_{dd}^{opt} \sim 2\text{-}4\text{ eV}$ (see, e.g., Ref. [9] and references therein) yield effective U 's which are sizeably less than typical $U_{dd} \sim 5\text{-}10\text{ eV}$, however, far from the so-called "negative- U " regime [8]. Yet Δ_{dd}^{opt} is a minimal energy cost of the optically excited d - d disproportionation or electron-hole formation due to a direct Franck-Condon (FC) CT transition. The question arises, what is the energy cost for the thermal excitation of such a local d - d disproportionation? The answer implies first of all the knowledge of the relaxation energy, or the energy gain due to the lattice polarization by the localized charges that can exceed 1 eV [10]. For instance, in insulating cuprates such as La_2CuO_4 the true (thermal) d - d charge transfer gap appears to be as small as 0.4-0.5 eV rather than 1.5-2.0 eV as derived from the optical gap measurements [5]. In other words, parent cuprates should be addressed to be d - d CT unstable systems.

At present, the CT instability with regard to the d - d disproportionation and formation of "negative- U " centers [8] is believed to be a rather typical property for a number of perovskite 3d transition-metal oxides such as CaFeO_3 , SrFeO_3 , RNiO_3 [11, 12], furthermore, in solid state chemistry one consider tens of disproportionated systems [13].

Classical disproportionation seems to be observed in the perovskite ferrate CaFeO_3 , where the average formal valence of the iron ion is Fe^{4+} ($3d^4$) is known to show a gradual charge disproportionation $2\text{Fe}^{4+} \rightarrow \text{Fe}^{3+} + \text{Fe}^{5+}$ below 290 K with antiferromagnetism

below 115 K according to Mössbauer studies [14]. The single magnetic hyperfine pattern for isostructural ferrate SrFeO_3 at 4 K, on the other hand, indicates seemingly a rapid electron exchange between Fe^{3+} and Fe^{5+} ions, and the hyperfine field coincides approximately with the average value of the corresponding parameters for CaFeO_3 . Probably, in this $3d^4$ oxide we meet with a manifestation of quantum effects and formation of a quantum dimerized phase such as a "valence bond solid" composed of S- or P-type *neutral* dimers described by wave functions:

$$\frac{1}{\sqrt{2}} \left[\Psi_1(3d^{m+1})\Psi_2(3d^{m-1}) \pm \Psi_1(3d^{m-1})\Psi_2(3d^{m+1}) \right],$$

respectively. The ^{57}Fe Mössbauer measurements point to a charge disproportionation in $\text{Sr}_3\text{Fe}_2\text{O}_7$, which has a double-layered perovskite structure [15].

Rare earth nickelates RNiO_3 (R is a trivalent rare earth ion) exhibit a first order metal-insulator phase transition (MIT) upon cooling with distinct signatures of the charge disproportionation [12, 16]. At $T_N \leq T_{MIT}$ these exhibit a further transition to a long-range antiferromagnetic ordered state with a nonzero magnetic moment for one of the two nonequivalent Ni sites [17]. A clear fingerprint of charge disproportionation is the breathing-type distortion of metal-oxygen octahedra since the different charge states of the transition-metal ion take different ionic radii (see, e.g., Ref. [12]).

However, a large body of 3d materials does not manifest the charge instability so clearly as $(\text{Ca},\text{Sr})\text{FeO}_3$ or RNiO_3 . For instance, the perovskite manganites RMnO_3 with the same as in ferrates $3d^4$ configuration of Mn^{3+} ions reveal a "hidden" CT instability [18, 19]. At first glance the disproportionation in manganese compounds is hardly possible since manganese atom does not manifest a "valence-skipping" phenomenon as, e.g. bismuth atom which can be found as Bi^{3+} or Bi^{5+} , but not Bi^{4+} , with a generic bismuth oxide BaBiO_3 to be a well-known example of a charge disproportionated system (see, e.g., Ref. [20] and references therein). However, strictly speaking, sometimes manganese reveals a valence preference, e.g., while both Mn^{2+} and Mn^{4+} are observed in MgO:Mn and CaO:Mn , the Mn^{3+} center is missing [21].

The reason for valence skipping or valence preference observed for many elements still remains a mystery. Recently, Harrison [22] has argued that most likely traditional lattice relaxation effects, rather than any intra-atomic mechanisms [8] (specific behavior of ionization energies, stability of closed shells, strong screening of the high-charged states) are a driving force for disproportionation with formation of "negative- U " centers.

Earlier it was argued that the disproportionated system can form an unconventional electron-hole Bose liquid whose phase diagram incorporates different phase states from classical, or chemical disproportionated state to quantum states, in particular, to the unconventional Bose-superfluid (superconducting) state [4]. Regrettably physicists have paid remarkably little attention to the problem of valence disproportionation and negative- U approaches ("chemical" route!) which are surely being grossly neglected in all present formal theoretical treatments of HTSC. Speaking about a close relation between disproportionation and superconductivity it is worth noting the text-book

example of BaBiO_3 system where we unexpectedly deal with the disproportionated $\text{Ba}^{3+} + \text{Ba}^{5+}$ ground state instead of the conventional lattice of Ba^{4+} cations [8]. The bismuthate can be converted to a superconductor by a nonisovalent substitution such as in $\text{Ba}^{2+}_{1-x}\text{K}^+_x\text{BiO}_3$. At present, this system seems to be the only one where the unconventional superconductivity is related anyhow with the disproportionation reaction.

In the paper we concern ourselves with great points of a so-called "disproportionation" scenario in 3d compounds which was addressed earlier by many authors, however, by now it was not properly developed as its consistent description in terms of conventional Hubbard type models is complicated, if any. Our final goal is to ascertain the criteria for a motivated search of the 3d systems which are the most promising ones as high-temperature superconductors. The paper is organized as follows. In Sec.II addressing a simple model of the CT unstable 2D system we demonstrate a potential of the disproportionation as a driving force for superconductivity. In Sec.III we analyze the features of the disproportionation reaction for different $3d^n$ pairs and do find $3d^n$ configurations optimal for the disproportionation driven superconductivity. In Sec.IV we address the electron structure of familiar 3d compounds with the optimal $3d^n$ configurations and point to high- T_c superconductivity observed in quasi-2D cuprates and iron pnictides/chalcogenides to be a result of the $d-d$ disproportionation. A short conclusion is made in Sec.V.

2. Simple toy model of the mixed valence system and the disproportionation driven superconductivity

2.1. Pseudospin description of the model mixed-valent system

Valent electronic states in strongly correlated 3d oxides manifest both significant correlations and $p-d$ covalency with a distinct trend to localisation of many-electron configurations formed by antibonding Me 3d-O 2p hybridized molecular orbitals. The localisation effects are particularly clear featured in the crystal field $d-d$ transitions whose spectra just weakly vary from diluted to concentrated 3d oxides. An optimal way to describe valent electronic states in strongly correlated 3d oxides is provided by quantum-chemical techniques such as the ligand field theory [23] which implies a crystal composed of a system of small 3d-cation-anion clusters. Naturally, such an approach has a number of shortcomings, nevertheless, this provides a clear physical picture of the complex electronic structure and the energy spectrum, as well as the possibility of a quantitative modelling. In a certain sense the cluster calculations might provide a better description of the overall electronic structure of insulating 3d oxides than different band structure calculations, mainly due to a better account for correlation effects and electron-lattice coupling.

In the 3d oxides with the disproportionation instability (1) we should consider as a minimum three different many-electron configurations, or different valent states,

with different types of the charge transfer. One strategy to deal with such a mixed-valence system is to create model pseudospin Hamiltonians which can reasonably well reproduce both the ground state and important low-energy excitations of the full problem. Standard pseudospin formalism represents a variant of the equivalent operators technique widely known in different physical problems from classical and quantum lattice gases, binary alloys, (anti)ferroelectrics,... to neural networks. The formalism starts with a finite basis set for a lattice site (triplet of M^0, M^\pm centers in our model, see below). Such an approach differs from well-known pseudospin-particle transformations akin Jordan-Wigner [24] or Holstein-Primakoff [25] transformation which establish a strict linkage between pseudospin operators and the creation/annihilation operators of the Fermi or Bose type. The pseudospin formalism for electron systems generally proceeds with a truncated basis and does not imply a strict relation to fermion operators that obey the fermionic anti-commutation rules.

To demonstrate the perspectives of the disproportionation in driving the superconductivity we address hereafter a simplified toy model of a mixed-valence system with three possible stable valence states of a cation-anion cluster (CuO_4 , MnO_6 , FeAs_4 ,...), hereafter M : M^0, M^\pm , forming the charge (isospin) triplet and neglect all other degrees of freedom saving only the quantum charge one. Similarly to the neutral-to-ionic electronic-structural transformation in organic charge-transfer crystals (see, e.g., paper by T. Luty in Ref. [26]) the system of charge triplets can be described in frames of the $S=1$ pseudo-spin formalism [4]. To this end we associate three different valence charge states of the M -center: M^0, M^\pm with three components of the $S = 1$ pseudo-spin (isospin) triplet with $M_S = 0, +1, -1$, respectively. Having in mind quasi-2D cuprates we associate M^0, M^\pm centers with three charge states of the CuO_4 plaquette: a bare center $M^0 = \text{CuO}_4^{6-}$, a hole center $M^+ = \text{CuO}_4^{5-}$, and an electron center $M^- = \text{CuO}_4^{7-}$, respectively.

However, the physically simple toy mixed-valence system should be described by rather complex effective pseudospin Hamiltonian as follows [4]

$$\begin{aligned} \hat{H} = & \sum_i (\Delta_i S_{iz}^2 - h_i S_{iz}) + \sum_{i<j} V_{ij} S_{iz} S_{jz} + \\ & \sum_{i<j} [D_{ij}^{(1)} (S_{i+} S_{j-} + S_{i-} S_{j+}) + D_{ij}^{(2)} (T_{i+} T_{j-} + T_{i-} T_{j+})] \\ & + \sum_{i<j} t_{ij} (S_{i+}^2 S_{j-}^2 + S_{i-}^2 S_{j+}^2), \end{aligned} \quad (2)$$

with a charge density constraint: $\frac{1}{2N} \sum_i \langle S_{iz} \rangle = \Delta n$, where Δn is the deviation from a half-filling ($N_{M^+} = N_{M^-}$). Two first single-site terms describe the effects of a bare pseudo-spin splitting, or the local energy of $M^{0,\pm}$ centers. The second term may be related to a pseudo-magnetic field $\mathbf{h}_i \parallel Z$, in particular, a real electric field which acts as a chemical potential. The third term describes the effects of the short- and long-range inter-site density-density interactions including screened Coulomb and covalent couplings. The last three kinetic energy terms in (2) describe the one- and two-particle

hopping, respectively ($T_{\pm} = \{S_z, S_{\pm}\}$). All the parameters have a clear physical meaning. The energy Δ_{CT} for the creation of uncoupled electron and hole centers, or effective parameter U_{dd} is: $\Delta_{CT} = 2\Delta$, while the energy Δ_{EH} for the creation of coupled electron and hole centers, or EH-dimer, is: $\Delta_{EH} = 2\Delta - V_{nn}$.

One should note that despite many simplifications, the effective pseudospin Hamiltonian (2) is rather complex, and represents one of the most general forms of the anisotropic $S = 1$ non-Heisenberg Hamiltonians. Its real spin counterpart corresponds to an anisotropic $S=1$ magnet with a single ion (on-site) and two-ion (bilinear and biquadratic) anisotropy in an external magnetic field. Spin Hamiltonian (2) describes an interplay of the Zeeman, single-ion and two-ion anisotropic terms giving rise to a competition of an (anti)ferromagnetic order along Z-axis with an in-plane XY magnetic order. Simplified versions of anisotropic $S = 1$ non-Heisenberg Hamiltonians have been investigated rather extensively in recent years [27, 28].

Our system is characterised by several order parameters. These are two classical (*diagonal*) order parameters: $\langle S_z \rangle$ being a valence, or charge density with an electro-neutrality constraint, and $\langle S_z^2 \rangle$ being the density of polar centers M^{\pm} , or "ionicity". In addition, there are two unconventional *off-diagonal* order parameters $\langle S_+ \rangle$ and $\langle T_+ \rangle$ related to two different types of a correlated single-particle transport, and one order parameter $\langle S_+^2 \rangle$ related to a two-particle transport. It is worth noting that the \hat{S}_+^2 operator creates an on-site hole pair, or composite boson, with a kinematic constraint $(\hat{S}_+^2)^2 = 0$, that underlines its "hard-core" nature. For real $S=1$ spin systems we deal with conventional "linear" magnetic order parameters $\langle S_z \rangle$ and $\langle S_+ \rangle$ related to diagonal (Z-) and off-diagonal (XY-) orderings and several spin-quadrupole order parameters: $\langle S_z^2 \rangle$, $\langle T_+ \rangle$, and $\langle S_+^2 \rangle$. Recently, the spin-quadrupole (spin-nematic) order $\langle S_+^2 \rangle$ has been investigated in Ref. [28].

The last three terms in (2) representing the one- and two-particle hopping, respectively, are of primary importance for the transport properties, and deserve special attention. Two types of one-particle hopping are governed by two transfer integrals $D^{(1,2)}$, respectively. The transfer integral $t'_{ij} = (D_{ij}^{(1)} + D_{ij}^{(2)})$ specifies the probability amplitude for a *local disproportionation, or the eh-pair creation*:

$$M^0 + M^0 \rightarrow M^{\pm} + M^{\mp},$$

and the inverse process of the *eh-pair recombination*:

$$M^{\pm} + M^{\mp} \rightarrow M^0 + M^0,$$

while the transfer integral $t''_{ij} = (D_{ij}^{(1)} - D_{ij}^{(2)})$ specifies the probability amplitude for a polar center transfer:

$$M^{\pm} + M^0 \rightarrow M^0 + M^{\pm},$$

or the *motion of the electron (hole) center in the lattice of M^0 -centers* or motion of the M^0 -center in the lattice of M^{\pm} -centers. It should be noted that, if $t''_{ij} = 0$ but $t'_{ij} \neq 0$, the

eh-pair is locked in a two-site configuration. The two-electron(hole) hopping is governed by the transfer integral t_{ij} that defines a probability amplitude for the exchange reaction:

$$M^{\pm} + M^{\mp} \rightarrow M^{\mp} + M^{\pm},$$

or the *motion of the electron (hole) center in the lattice of the hole (electron) centers*. It is worth noting that in the conventional Hubbard-like models all the types of one-electron(hole) transport are governed by the same transfer integral: $t'_{ij} = t''_{ij}$, while our model implies independent parameters for the disproportionation/recombination process and a simple quasiparticle motion on the lattice of M^0 -centers. In other words, we deal with a "correlated" single particle transport.

2.2. Electron-hole Bose liquid, hard-core composite bosons and superconductivity in disproportionated systems

Classical (or chemical) description of the mixed-valence systems implies a full neglect of the *off-diagonal* purely quantum CT effects: $D^{(1,2)} = t = 0$, hence the valence of any site remains to be definite: $0, \pm 1$, and we deal with a system of localized polar centers. Quantum description implies the taking account of the CT effects so that we arrive at *quantum superpositions of different valence states* resulting in an *indefinite* on-site valence and ionicity whose effective, or mean values $\langle S_z \rangle$ and $\langle S_z^2 \rangle$ can vary from -1 to $+1$ and 0 to $+1$, respectively.

Simple uniform mean-field phases of the mixed-valent system include an insulating monovalent M^0 -phase (parent phase), mixed-valence binary (disproportionated) M^{\pm} -phase, and mixed-valence ternary ("under-disproportionated") $M^{0,\pm}$ -phase [4].

Insulating monovalent M^0 -phase with $\langle S_z^2 \rangle = 0$ is a rather conventional ground state phase for various Mott-Hubbard insulators such as 3d oxides with a large enough positive magnitude of $\Delta > \Delta_{cr}$ parameter ($U > 0$). All the centers have the same bare M^0 valence state. Mixed-valence binary (disproportionated) M^{\pm} -phase with $\langle S_z^2 \rangle = 1$ implies an overall disproportionation $M^0 + M^0 \rightarrow M^{\pm} + M^{\mp}$. It is a rather unconventional phase for insulators. All the centers have the "ionized" valence state, one half the M^+ state, and another half the M^- one, though one may in common conceive of a deviation from the half-filling. A simplified "chemical" approach to M^{\pm} -phase as to a classical disproportionated phase is widely spread in solid state chemistry [13]. Typical ground state of such a classical phase corresponds to a checkerboard charge order, or longitudinal antiferromagnetic (staggered) pseudospin Ising-like Z-ordering. In systems with a short-range density-density coupling V_{nn} the disproportionation phase transition $M^0 \rightarrow M^{\pm}$, or pseudospin reorientation occurs, if $\Delta < \Delta_{cr} = \frac{z}{2}V_{nn}$, where z is a number of nearest neighbours. In other words, the charge transfer instability of the parent M^0 -phase implies not only negative but also small enough positive $\Delta_{CT} = U_{dd}$.

The mixed valence M^{\pm} phase as a system of strongly correlated electron and hole centers appears to be equivalent to a Bose-liquid in contrast with the electron-hole Fermi-liquid in conventional semiconductors, hence it can be termed as *electron-hole*

Bose liquid (EHL) [4, 5, 19]. Indeed, one may address the electron M^- center to be a system of a local composite boson (e^2) localized on the hole M^+ center: $M^- = M^+ + e^2$.

Three well known molecular-field uniform phase states of the M^\pm binary mixture, or EHL phase can be specified as follows:

- i) charge ordered (CO) insulating state with $\langle S_z \rangle = \pm 1$ and zero modulus of bosonic off-diagonal order parameter: $|\langle S_+^2 \rangle| = 0$;
- ii) Bose-superfluid (BS) superconducting state with $\langle S_z \rangle = 0$, $\langle S_+^2 \rangle = e^{2i\phi}$;
- iii) mixed Bose-superfluid-charge ordering (BS+CO) superconducting state (supersolid) with $0 < |\langle S_z \rangle| < 1$, $\langle S_+^2 \rangle \neq 0$.

In addition, we should mention the high-temperature non-ordered (NO) Bose-metallic phase with $\ll S_z \gg = 0$.

Disproportionation in such oxides as (Ca,Sr)FeO₃, RNiO₃ yields an electron-hole Bose system with the 50% concentration of the composite bosons, or the half-filling. At variance with the parent quasi-2D cuprates the disproportionated 3d oxides from the very beginning can be addressed to be "negative- U ", or M^\pm systems with $\Delta < \Delta_{cr}$ where the superconductivity can be driven by a deviation from the half-filling.

How a typical insulating parent 3d M^0 -system, such as La₂CuO₄, can be driven to the disproportionated M^\pm , or EHL phase? Simplest way is the hole/electron doping due to a nonisovalent substitution (NIS), that does solve two problems at once. First, it creates the impurity centers for a local condensation of the EH dimers, or pairs of M^\pm -centers thus shifting the system to the "negative- U " regime. Second, the doping in cuprates such as La_{2-x}Sr_xCuO₄ and Nd_{2-x}Ce_xCuO₄ gradually shifts the M^\pm -phase away from half-filling making the concentration of the local S-bosons to be $n_B = 0.5 - x/2$ (LSCO) or $n_B = 0.5 + x/2$ (NCCO) thus promoting the superconductivity. In both the hole- and electron-doped cuprates we deal with composite S-bosons moving on the lattice of the hole centers CuO₄⁵⁻, that makes the unconventional properties of the hole centers [29, 30] to be common ones for the both types of cuprates. It is clear that the disproportionation scenario makes the doped cuprates the objects of *bosonic* physics. Obviously, the appearance of an inhomogeneous impurity potential under nonisovalent substitution deforms the phase diagram typical for uniform systems, in particular, in the "underdoped" regime where the system transforms from the parent phase M^0 into the disproportionated phase M^\pm .

In the limit $\Delta \rightarrow -\infty$, the EHL phase is equivalent to the lattice hard-core (hc) Bose system with an inter-site repulsion whose Hamiltonian can be written in a standard form as follows (see Refs.[31, 32] and references therein):

$$H_{hc} = - \sum_{i>j} t_{ij} \hat{P}(\hat{B}_i^\dagger \hat{B}_j + \hat{B}_j^\dagger \hat{B}_i) \hat{P} + \sum_{i>j} V_{ij} N_i N_j - \mu \sum_i N_i, \quad (3)$$

where \hat{P} is the projection operator which removes double occupancy of any site. Here $\hat{B}^\dagger(\hat{B})$ are the Pauli creation (annihilation) operators which are Bose-like commuting for different sites $[\hat{B}_i, \hat{B}_j^\dagger] = 0$, if $i \neq j$, $[\hat{B}_i, \hat{B}_i^\dagger] = 1 - 2N_i$, $N_i = \hat{B}_i^\dagger \hat{B}_i$; N is a full number of sites. μ the chemical potential determined from the condition of fixed full number of

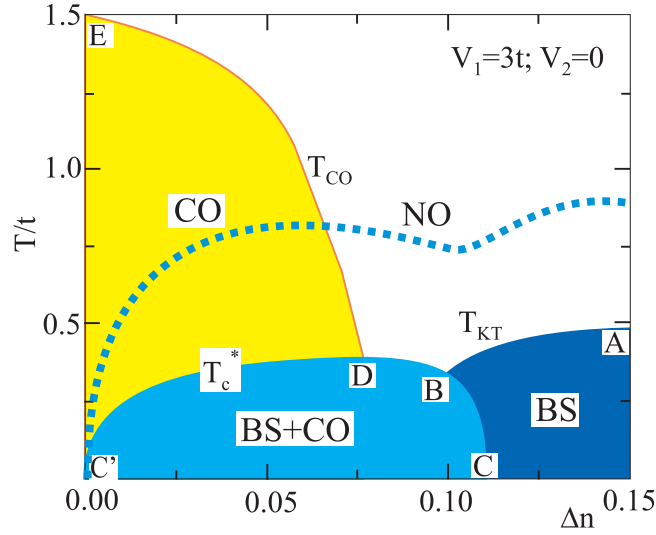


Figure 1. (Color online) The QMC T-n phase diagram of the 2D hard-core boson system (reconstruction of Fig.2 from Ref.[34], $V_1 = V_{nn}, V_2 = V_{nnn}$). Dotted line schematically circumscribes the region of the well developed BS+CO and BS superconducting fluctuations (local supercurrent response) giving rise to anomalous Nernst and local diamagnetism signals.

bosons $N_l = \sum_{i=1}^N \langle N_i \rangle$ or concentration $n = N_l/N \in [0, 1]$. The t_{ij} denotes an effective transfer integral, V_{ij} is an intersite interaction between the bosons. It is worth noting that near half-filling ($n \approx 1/2$) one might introduce the renormalization $N_i \rightarrow (N_i - 1/2)$, or neutralizing background, that immediately provides the particle-hole symmetry.

The model of hard-core bosons with an intersite repulsion as a minimal model of the EH Bose liquid can be mapped to a system of pseudospins $s=1/2$ exposed to an external magnetic field in the Z-direction (Matsubara-Matsuda transformation [33]). For the system with a neutralizing background we arrive at an effective pseudo-spin Hamiltonian

$$H_{hc} = \sum_{i>j} J_{ij}^{xy} (\hat{s}_i^+ \hat{s}_j^- + \hat{s}_j^+ \hat{s}_i^-) + \sum_{i>j} J_{ij}^z \hat{s}_i^z \hat{s}_j^z - \mu \sum_i \hat{s}_i^z, \quad (4)$$

where $J_{ij}^{xy} = 2t_{ij}$, $J_{ij}^z = V_{ij}$, $\hat{s}^- = \frac{1}{\sqrt{2}}\hat{B}$, $\hat{s}^+ = -\frac{1}{\sqrt{2}}\hat{B}^\dagger$, $\hat{s}^z = -\frac{1}{2} + \hat{B}_i^\dagger \hat{B}_i$, $\hat{s}^\pm = \mp \frac{1}{\sqrt{2}}(\hat{s}^x \pm i\hat{s}^y)$.

In terms of the $s=1/2$ pseudospins the non-ordered NO, or liquid phase, corresponds to a paramagnetic phase, Bose superfluid BS order does to a magnetic order in the XY plane, while charge density order CO does to a magnetic order in the Z direction.

In Fig.1 we present the phase diagram of the square lattice hc-boson Hubbard model with the nearest neighbour (nn) transfer integral $t_{nn} = t$ (the Josephson coupling) and repulsion $V_{nn} = 3t$, derived from the quantum Monte-Carlo (QMC) calculations by Schmid *et al.* [34] (see, also Ref. [31]). Different filling points to CO phase, BS phase, and phase separated supersolid BS+CO phase. The AB line $T_{KT}(x)$ points to 2D Kosterlitz-Thouless phase transition; the C-B-D-C' line points to the first order phase transition;

the D-E line $T_{CO}(\Delta n)$ which can be termed as the pseudogap onset temperature $T^*(\Delta n)$ points to the second order Ising kind melting phase transition CO-NO into a nonordered, or normal fluid phase. At half-filling ($n_B = 0.5, \Delta n = 0$) the system obviously prefers a checkerboard charge order (Néel antiferromagnetic order in the Z -direction below $T_{CO} = 0.567 V_{nn}$ given $t = 0$).

It is worth noting that the phase diagram in Fig.1 greatly resembles that of typical for doped quasi-2D cuprates [35] truly reproducing many important aspects of the normal and superconducting state, in particular, the pseudogap-like effects of the charge ordering and various signatures of the local superconductivity, that explain the anomalous Nernst [36] and local diamagnetism signals [37].

2.3. Topological phase separation in the 2D hard-core Bose system

It is worth noting that all the lines in the phase diagram of the 2D hard-core Bose system in Fig. 1 point only to long range orders and do not concern the intricate intrinsic inhomogeneity. However, the CO state was shown [32] to be unstable with regard to a so-called CO+BS topological phase separation under doping, or deviation from the half-filling. The boson addition or removal in the half-filled hard-core boson system is assumed to be a driving force for a nucleation of a multi-center skyrmion-like self-organized collective mode that resembles a system of CO bubble domains with a Bose superfluid and extra bosons both confined in domain walls. The antiphase domain wall in the CO bubble domain appears to be a very efficient ring-shaped potential well for the localization of a single extra boson (or bosonic hole) thus forming a novel type of a topological defect with a neutral or single-charged ($q=2e$) domain wall. Such a *topological CO+BS phase separation*, more than likely being the dynamical one, rather than an uniform mixed CO+BS supersolid phase predicted by the mean-field approximation [31], is believed to describe the evolution of hc-BH model away from half-filling.

Fig. 2 presents the schematic view of the smallest neutral skyrmion-like bubble domain in a checkerboard CO phase for a 2D square lattice with an effective size of the three lattice spacings ($\sim 12 \text{ \AA}$) [32]. The domain wall is believed to include as a minimum eight sites forming a ring-shaped system of four dimers each composed of two sites. There are two types of the domains which differ by a rotation by $\pm\pi/2$. Such a charged topological defect can be addressed as an extended ($q = \pm 2e$) skyrmion-like mobile quasiparticle. On the other hand, the bubble seems to be a peculiar quantum of a "local superconductivity".

The bubble domain may be addressed to be well isolated only if its close surrounding does not contain another domain(s) which could be involved to a "dangerous" frustrating overlap. Each domain in Fig.2 has $z = 12$ of such neighbors. Hence the concentration of well isolated domains can be written as follows: $P_0(\Delta n) = |\Delta n|(1 - |\Delta n|)^z$, where z is a number of "dangerous" neighbors, Δn the doped boson concentration. The $P_0(\Delta n)$ maximum is reached at $\Delta n_0 = \frac{1}{z+1}$. In our case $\Delta n_0 = 1/13$, or ≈ 0.077 . With increasing

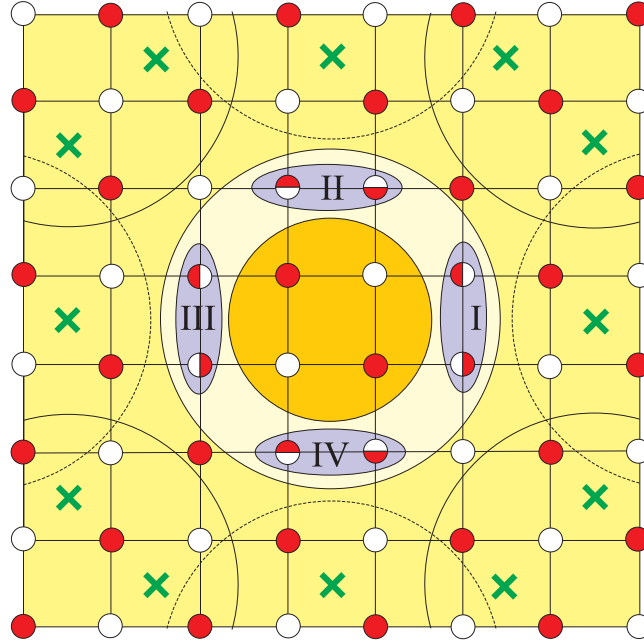


Figure 2. Skyrmion-like bubble domain in the checkerboard CO phase with the eight site ring-shaped domain wall. Electron (M^-) and hole (M^+) centers are marked by different filling. The four dimers within the domain wall are marked by I-IV. Their specific filling points to a bond-centered CO in the domain wall rather than a site-centered CO in the domain. Schematically shown are nearest and next-nearest neighbor domains which do not overlap with the central domain. Centers of all the 12 nearest neighbor domains which could be involved to a "dangerous" frustrating overlap with the central domain are marked by crosses.

doping the deviation of $P_0(\Delta n)$ from the linear law rises. On the other hand, knowing the effective domain area $S_d \approx 9a^2$ we can roughly estimate the limiting concentration of the single-domain model description to be $\Delta n_{max} \approx 1/9 \approx 0.11$.

The bubble's system is believed to reveal many properties typical for granular superconductors, CDW materials, Wigner crystals, and multi-skyrmion system akin in a quantum Hall ferromagnetic state of a 2D electron gas [32]. The concept of a static or dynamic bubble system introduces a large body of novelties into the physics of the EH Bose liquid related to a complex intra-bubble structure, bubble transport, bubble-bubble coupling, novel excitation modes, pinning of the bubble system etc. From a viewpoint of the novel charge order effects we point to an evolution of the bubble system upon lowering the temperature which implies a sequence of the isotropic liquid phase, the liquid-crystal phase, and the incommensurate bubble crystal phase with a quantum melting effect near the "magic" doping level, e.g. $\Delta n_b = 1/16$, where the bubble lattice undergoes the structural phase transition. It is worth noting that the bubble crystallization is accompanied by different (pseudo)gap effects. From a viewpoint of the off-diagonal BS order we should point to a step-by-step formation of the local BS condensate starting with an intra-EH-dimer order at $kT \sim t_{nn}$, an intra-bubble order

at $kT \sim t_{nnn}$, a short-range bubble order at $kT \sim t_{bb}$ (t_{bb} is a bubble transfer integral), formation of extended quasi-1D clusters which can undergo a transition to a phase-coherent state (filamentary or gossamer superconductivity [38]). Finally, upon the rise of the number of such clusters, the prerequisites for a percolative 2D and bulk 3D superconductivity are created. Attractively large temperatures of the emergence of the nonzero local BS condensate density engender different reasonable speculations as regards its practical realization.

The topologically inhomogeneous phase of the hc-BH system away from the half-filling can exhibit the signatures both of s -, d -, and p -symmetry of the off-diagonal order [32]. The model allows us to study subtle microscopic details of the order parameter distribution including its symmetry in a real rather than momentum space, though the problem of the structure and stability of nanoscale domain configurations remains to be solved.

It is worth noting that the bubble model predicts the optimal conditions for 2D and 3D superconductivity in the doped cuprates at $x_{opt} \approx 2\Delta n_0 \approx 0.154$ and a suppression of superconductivity at $x > 2\Delta n_{max} \approx 0.22$. On the other hand, the bubble model predicts a so-called "self-doping" (SD) mechanism of superconductivity in "negative- U ", or M^\pm systems. Such a mechanism is realized when the CO phase in the system appears to be unstable with regard to a nucleation of positively and negatively charged bubbles preserving a charge neutrality. Probably, such a "self-doping" explains the superconductivity in $\text{YBa}_2\text{Cu}_4\text{O}_8$ [39] and LiFeAs [40].

It should be noted that the bubble system can manifest two types of the dispersive features that reflect a dominance of the kinetic energy (the bubble transfer) or the potential energy (the bubble-bubble coupling), respectively. Indeed, a single mobile bubble has energy $\varepsilon(\mathbf{q})$, while different static bubble crystal configurations (Wigner electronic crystals) can be specified by the quasimomentum \mathbf{q} and corresponding energy $E(\mathbf{q})$.

3. Disproportionation and local composite bosons in $3d^n$ systems

3.1. Local composite bosons in $3d^n$ systems

As we have seen above the disproportionation

$$3d^n + 3d^n \rightarrow 3d^{n+1} + 3d^{n-1}$$

is addressed to be a candidate mechanism to drive the superconductivity in nominally insulating $3d$ compounds. A simple view of the disproportionated system implies the electron(hole) center $3d^{n+1}(3d^{n-1})$ to be composed of hole(electron) center plus electron(hole) coupled pair $3d^2(3\bar{d}^2)$ that seems to constitute a composite electron(hole) local boson. In other words, the disproportionated system is anticipated to be a system of local bosons moving in a lattice formed by electron(hole) centers. The disproportionation scenario implies the composite local boson to be anyhow an integral

part of a stable many-electron atomic configuration, $3d^{n+1}$ or $3d^{n-1}$. Microscopic nature of the "attractive force which could overcome the natural Coulomb repulsion between two electrons which constitute a Bose pair" [41] evolves both from main intra-atomic correlations and electron-lattice polarisation effects [22] providing the stability of $3d^{n\pm 1}$ configurations.

However, for the representation of local composite bosons to justify we should take into account some rather strict limitations imposed by the orbital structure of the 3d states and the genealogy of many-electron $3d^{n,n\pm 1}$ states. First of all, the effective two-particle two-site transfer integrals

$$\langle 3d_1^{n+1} 3d_2^{n-1} | \hat{H} | 3d_1^{n-1} 3d_2^{n+1} \rangle ,$$

that describe the exchange reaction

$$3d^{n+1} + 3d^{n-1} \rightarrow 3d^{n-1} + 3d^{n+1}$$

are due to reduce to a simple form

$$\langle 3d_1^{n+1} 3d_2^{n-1} | \hat{H} | 3d_1^{n-1} 3d_2^{n+1} \rangle = \langle 3d_1^2 | \hat{H} | 3d_2^2 \rangle = t_{12}$$

we need to introduce directly the local boson representation. The two-particle transfer integral t_{12} is a main parameter that governs both the transport and superconducting perspectives of the disproportionated system. It can be written as follows:

$$t_{12} = \langle 20 | V_{ee} | 02 \rangle - \sum_{11} \frac{\langle 20 | \hat{h} | 11 \rangle \langle 11 | \hat{h} | 02 \rangle}{\Delta_{dd}} ,$$

where the first term describes a simultaneous tunnel transfer of the electron pair due to the Coulomb coupling V_{ee} and may be called as a "potential" contribution, whereas the second describes a two-step (20-11-02) electron-pair transfer via successive one-electron transfer due to the one-electron Hamiltonian \hat{h} , and may be called as a "kinetic" contribution. The value of the composite boson transfer integral is closely related to that of the exchange integral, i.e. $t_{12} \approx J_{12}$.

Justification of the local composite boson implies a specific genealogy of the many-electron states $\Psi(3d^{n+1})$ and $\Psi(3d^{n-1})$: the wave functions should have a simple structure

$$\Psi(3d^{n+1}) = \Psi(3d^2)\Psi(3d^{n-1}), \quad \Psi(3d^{n-1}) = \Psi(3d^2)\Psi(3d^{n+1}) \quad (5)$$

in electron, or hole representation, respectively. To gain more insight into the main features of the disproportionation reaction hereafter we analyze the d - d CT transition $3d^n + 3d^n \rightarrow 3d^{n+1} + 3d^{n-1}$ in strongly correlated 3d systems with a high (octahedral, tetrahedral, and cubic) local symmetry. For crystal field configurations such as $t_{2g}^{n_1} e_g^{n_2}$ the optimal disproportionation scheme (5) implies single configurations both for $\Psi(3d^{n+1})$ and $\Psi(3d^{n-1})$. It is easy to see that the optimal conditions for the superconductivity are expected for parent $3d^n$ systems with $3d^{n\pm 1}$ configurations which correspond either

empty, or filled and half-filled t_{2g} and e_g orbitals. Second, to minimize the reduction effect of the electron-lattice interaction and avoid the localization, we need the S -type (A_{1g}, A_{2g}) orbital symmetry of the local boson that provides the conservation of the orbital degeneracy when it moves on the lattice. Third, to minimize the reduction effect of the spin degrees of freedom, we need spin-singlet local bosons. Fourth, to maximize the transfer integral we need a participation of the strongest σ bonds. In other words, we should point to a specific role of the one-electron orbitals forming the two-electron boson state. Furthermore, the optimized ground state of the local boson should be well isolated, that is separated from excited states by a gap on the order of 1 eV. In any case, along with the electron-lattice polarisation effects which stabilize the $3d^{n\pm 1}$ configurations and minimize the CT energy, the many-electron configuration, intra-atomic correlations, force and symmetry of the crystal field seem to be most important factors of the disproportionation scenario. All the above constraints restrict strongly the number of $3d^n$ systems to be candidates for the high- T_c superconducting materials in frames of the disproportionation scenario.

3.2. Optimal disproportionation schemes for different $3d^n$ ions in high-symmetry crystal field

Below we address the optimal disproportionation schemes for different $3d^n$ ions in high-symmetry crystal field. It is worth noting that for *octahedral* or *tetrahedral* (cubic) crystal field the electron filling starts with the t_{2g} or e_g orbitals, respectively. Depending on the relation between the crystal field and intra-atomic correlation energies we will consider either high-spin (HS) or low-spin (LS) complexes such as MeO_6 or MeO_4 in $3d$ oxides.

$3d^1$ ions (Ti^{3+} , V^{4+}). Disproportionation $3d^1 + 3d^1 \rightarrow 3d^0 + 3d^2$ gives rise to a system of local composite bosons, or electron pairs $3d^2$, moving in a lattice formed by the $3d^0$ centers. Simplest electronic configuration $3d^1$ is realized as t_{2g}^1 configuration for octahedral or e_g^1 configuration for the cubic or tetrahedral crystal field. For the t_{2g}^2 configuration we arrive at an orbital and spin triplet ground state ${}^3T_{1g}$ with seemingly no optimistic expectations as regards the superconductivity. Some perspectives may be related to a spin-orbital coupling V_{SO} that stabilizes a singlet state with a net momentum $J=0$, though the electron-lattice interaction can destroy spin-orbital coupling giving rise to an Jahn-Teller polaron. More attractive expectations are related to the e_g^2 configuration in the tetrahedral crystal field when we arrive at an S-like though spin-triplet ground state ${}^3A_{2g}$. In other words, there appears an opportunity to realize an unconventional system of spin-triplet local S-like bosons moving on the electronically "inactive" lattice (see Fig. 1).

$3d^2$ ions (V^{3+} , Cr^{4+}). Two-electron configuration $3d^2$ is realized as t_{2g}^2 configuration for octahedral or e_g^2 configuration for the cubic or tetrahedral crystal field. Disproportionation $3d^2 + 3d^2 \rightarrow 3d^1 + 3d^3$ seems to give rise to a system of electron pairs $3d^2$, or local composite bosons, moving in a lattice formed by the $3d^1$ centers. However,

the genealogy of the low-spin $e_g^3; {}^2E_g$ configuration does not permit the insertion of a well defined composite boson. Indeed, the genealogical link of the e_g^3 and e_g^1 configurations reads as follows:

$$\begin{aligned} |e_g^3; {}^2E_g\rangle &= \frac{1}{\sqrt{6}} |(e_g^2)^1 A_{1g}; e_g^1; {}^2E_g\rangle - \frac{1}{\sqrt{3}} |(e_g^2)^1 E_g; e_g^1; {}^2E_g\rangle \\ &- \frac{1}{\sqrt{2}} |(e_g^2)^3 A_{2g}; e_g^1; {}^2E_g\rangle, \end{aligned} \quad (6)$$

and implies a participation of not one but three different terms of the e_g^2 configuration. Genealogy of the high-spin $t_{2g}^3; {}^4A_{2g}$ configuration obeys the master condition (see Exp.(2)) that permits the formation of a well defined composite boson with HS-configuration $t_{2g}^2; {}^3T_{1g}$. It means that the disproportionation reaction

$$t_{2g}^2 + t_{2g}^2 \rightarrow t_{2g}^1 + t_{2g}^3$$

gives rise to a system of the local electron type bosons (t_{2g}^2) on the lattice with the on-site t_{2g}^1 configuration or hole type bosons (\bar{t}_{2g}^2) on the lattice with the on-site HS- $t_{2g}^3; {}^4A_{2g}$ configuration. However, in any case such a composite boson appears to be charged by both spin and orbital degrees of freedom, in addition, this is prone to move on the lattice with a spin or spin and orbital degeneracy that strongly restricts "superconducting perspectives". Some hopes may be related to a spin-orbital coupling V_{SO} that stabilizes a singlet state with a net momentum $J=0$, though the electron-lattice interaction will compete with the spin-orbital coupling giving rise to an Jahn-Teller polaron.

3d³ ions (V^{2+} , Cr^{3+} , Mn^{4+}). Three-electron configuration $3d^3$ is realized as t_{2g}^3 configuration for octahedral, e_g^3 or $e_g^2 t_{2g}$ configuration for strong or weak tetrahedral or cubic crystal field, respectively. However, the local boson representation can be introduced only for tetrahedral/cubic high-spin configuration:

$$e_g^2 t_{2g} + e_g^2 t_{2g} \rightarrow e_g^2 + e_g^2 t_{2g}^2$$

when the disproportionated system can be addressed to be a system of $t_{2g}^2; {}^3T_{1g}$ local composite bosons on the lattice with the on-site $e_g^2; {}^3A_{2g}$ 3d-configuration. Obviously, we arrive at delusive perspectives for the high- T_c superconductivity.

3d⁴ ions (Mn^{3+} , Cr^{2+} , Fe^{4+}). The electron configuration near the half-filling, $3d^4$, is particularly interesting given the *octahedral* crystal field. Then the high-spin (Hund) $3d^4$ configuration disproportionates as follows:

$$(t_{2g}^3 e_g^1; {}^5E_g) + (t_{2g}^3 e_g^1; {}^5E_g) \rightarrow (t_{2g}^3; {}^4A_{2g}) + (t_{2g}^3 e_g^2; {}^6A_{1g}), \quad (7)$$

where $(t_{2g}^3 e_g^2; {}^6A_{1g}) = (t_{2g}^3; {}^4A_{2g}) \times (e_g^2; {}^3A_{2g})$. In other words, the disproportionated system can be viewed as a system of spin-triplet composite electron bosons $(e_g^2; {}^3A_{2g})$ moving in the lattice composed of the localized hole spin-3/2 S-type $(t_{2g}^3; {}^4A_{2g})$ centers (see Fig.1). Interestingly that we can address the system in other way to be a system of spin-triplet composite hole bosons $(\bar{e}_g^2; {}^3A_{2g})$ moving in the lattice composed of the localized electron spin-5/2 S-type $(t_{2g}^3 e_g^2; {}^6A_{1g})$ centers. It is worth noting that the

electron-type boson obeys a conventional (ferromagnetic) Hund rule on lattice sites while the hole-type boson obeys an unconventional (antiferromagnetic) "anti"-Hund rule on lattice sites. Local composite bosons can be formed also for the low-spin octahedral or high-spin tetrahedral d^4 systems, however, we arrive at the composite boson with a $t_{2g}^2; ^3T_{1g}$ or $\bar{t}_{2g}^2; ^3T_{1g}$ configuration and a spin-3/2 or 5/2 lattice.

$3d^5$ ions (Fe^{3+} , Mn^{2+}). The low-spin $3d^5$ configuration appears to be near filling both in *octahedral* and *tetrahedral* crystal field when it disproportionates as follows:

$$(t_{2g}^5) + (\bar{t}_{2g}^5) \rightarrow (t_{2g}^4; ^3T_{1g}) + (t_{2g}^6; ^1A_{1g}) \quad (8)$$

or

$$(e_g^4 t_{2g}^1) + (e_g^4 \bar{t}_{2g}^1) \rightarrow (e_g^4; ^1A_{1g}) + (e_g^4 t_{2g}^2; ^3T_{1g}) \quad (9)$$

where $(t_{2g}^4; ^3T_{1g}) = (t_{2g}^2; ^3T_{1g}) \times (t_{2g}^6; ^1A_{1g})$. In other words, the disproportionated system given the *octahedral* crystal field can be viewed as a system of spin and orbital triplet composite hole bosons $(t_{2g}^2; ^3T_{1g})$ moving in a lattice composed of the spinless S-type $((t_{2g}^6; ^1A_{1g}))$ centers. Given *tetrahedral* crystal field we arrive at a system of spin and orbital triplet composite electron bosons $(t_{2g}^2; ^3T_{1g})$ moving in a lattice composed of the spinless S-type $((e_g^4; ^1A_{1g}))$ centers. Orbital degeneracy of the local bosons can give rise to the formation of the JT polarons followed by its localization.

$3d^6$ ions (Fe^{2+} , Co^{3+}). In this case the specific genealogy (5) of polar $3d^{n\pm 1}$ centers can be realized only for high-spin (Hund) configuration. In *tetrahedral* or *cubic* crystal field the $3d^6$ system disproportionates as follows:

$$(e_g^3 t_{2g}^3; ^5E_g) + (e_g^3 \bar{t}_{2g}^3; ^5E_g) \rightarrow (e_g^2 t_{2g}^3; ^6A_{1g}) + (e_g^4 t_{2g}^3; ^4A_{2g}), \quad (10)$$

where $(e_g^2 t_{2g}^3; ^6A_{1g}) = (e_g^4 t_{2g}^3; ^4A_{2g}) \times (\bar{e}_g^2; ^3A_{2g})$. In other words, the disproportionated system can be viewed as a system of spin-triplet composite hole bosons $(\bar{e}_g^2; ^3A_{2g})$ moving in the lattice composed of the electron $S=3/2$ $(e_g^4 t_{2g}^3; ^4A_{2g})$ centers. We can address the system in other way to be a system of spin-triplet composite electron bosons $(e_g^2; ^3A_{2g})$ moving in the lattice composed of the localized hole spin-5/2 S-type $(e_g^2 t_{2g}^3; ^6A_{1g})$ centers (see Fig. 1). The situation resembles that of the Hund $3d^4$ electron configuration given the *octahedral* crystal field.

In octahedral crystal field the HS- $3d^6$ system disproportionates as follows:

$$(t_{2g}^4 e_g^2; ^5T_{2g}) + (t_{2g}^4 \bar{e}_g^2; ^5T_{2g}) \rightarrow (t_{2g}^3 e_g^2; ^6A_{1g}) + (t_{2g}^5 e_g^2; ^4T_{1g}). \quad (11)$$

The disproportionated system can be viewed as a system of spin-triplet composite electron-type bosons $(t_{2g}^2; ^3T_{1g})$ moving in the lattice composed of the hole $S=5/2$ $t_{2g}^3 e_g^2; ^6A_{1g}$ centers. Orbital degeneracy for the composite boson implies a competition of the vibronic JT coupling and the kinetic energy.

$3d^7$ ions (Ni^{3+} , Co^{2+}). For low-spin (non-Hund) configuration in *octahedral* crystal field the $3d^7$ system disproportionates as follows:

$$(t_{2g}^6 e_g^1; ^2E_g) + (t_{2g}^6 \bar{e}_g^1; ^2E_g) \rightarrow (t_{2g}^6; ^1A_{1g}) + (t_{2g}^6 e_g^2; ^3A_{2g}), \quad (12)$$

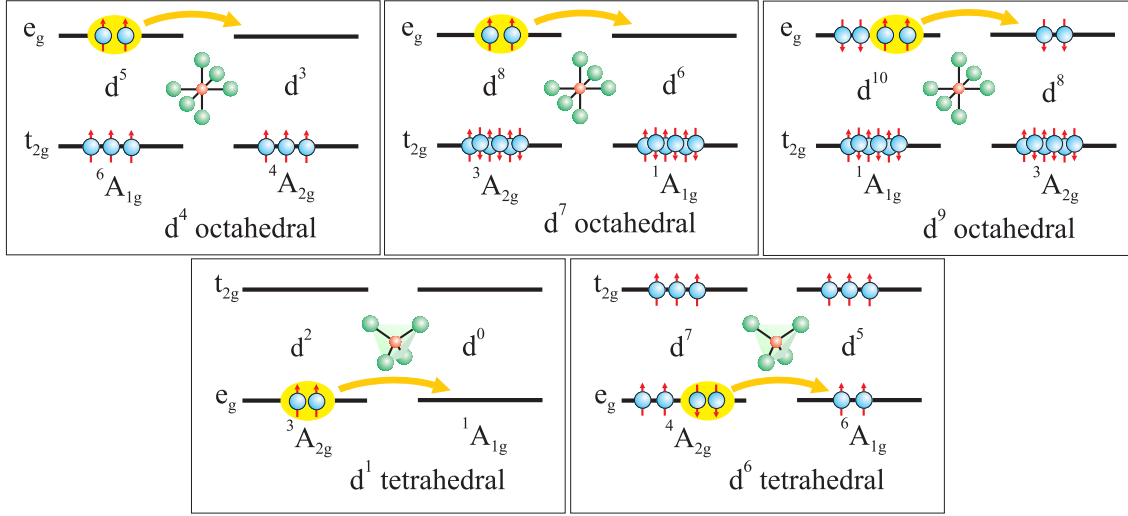


Figure 3. (Color online) Disproportionation schemes for the high-symmetry crystal field which are believed to provide optimal conditions for the disproportionation driven superconductivity.

where $(t_{2g}^6 e_g^2; {}^3A_{2g}) = (t_{2g}^6; {}^1A_{1g}) \times (e_g^2; {}^3A_{2g})$. In other words, the disproportionated system can be viewed as a system of spin-triplet composite electron bosons $(e_g^2; {}^3A_{2g})$ moving in the lattice composed of the hole $S=0$ $(t_{2g}^6; {}^1A_{1g})$ centers (see Fig. 1).

For high-spin (Hund) configuration in *octahedral* crystal field the $3d^7$ system disproportionates as follows:

$$(t_{2g}^5 e_g^2; {}^4T_{1g}) + (t_{2g}^5 e_g^2; {}^4T_{1g}) \rightarrow (t_{2g}^4 e_g^2; {}^5T_{2g}) + (t_{2g}^6 e_g^2; {}^3A_{2g}), \quad (13)$$

The disproportionated system can be viewed as a system of spin-triplet composite hole bosons $t_{2g}^2; {}^3T_{1g}$ moving on the lattice composed of the electron $S=1$ $(t_{2g}^6 e_g^2; {}^3A_{2g})$ centers.

$3d^8$ ions (Ni^{2+} , Cu^{3+}). For the ground state configuration in *octahedral* crystal field the $3d^8$ system disproportionates as follows:

$$(t_{2g}^6 e_g^2; {}^3A_{2g}) + (t_{2g}^6 e_g^2; {}^3A_{2g}) \rightarrow (t_{2g}^6 e_g^1; {}^2E_g) + (t_{2g}^6 e_g^3; {}^2E_g), \quad (14)$$

with the formation of the two Jahn-Teller centers which are prone to a vibronic localization. However, the genealogy of the $e_g^3; {}^2E_g$ configuration does not permit the insertion of the well defined composite boson (see Exp.6). The $3d^8$ system given the *tetrahedral* crystal field disproportionates as follows:

$$(e_g^4 t_{2g}^4; {}^3T_{1g}) + (e_g^4 t_{2g}^4; {}^3T_{1g}) \rightarrow (e_g^4 t_{2g}^3; {}^4A_{2g}) + (e_g^4 t_{2g}^5; {}^2T_{2g}), \quad (15)$$

In other words, such a disproportionated system can be viewed as a system of spin-triplet composite electron-type JT bosons $(t_{2g}^2; {}^3T_{1g})$ moving on the lattice composed of the hole spin-3/2 $(e_g^4 t_{2g}^3; {}^4A_{2g})$ S-type centers.

$3d^9$ ions (Cu^{2+}). In *octahedral* crystal field the $3d^9$ system disproportionates as follows:

$$(t_{2g}^6 e_g^3; {}^2E_g) + (t_{2g}^6 e_g^3; {}^2E_g) \rightarrow (t_{2g}^6 e_g^2; {}^3A_{2g}) + (t_{2g}^6 e_g^4; {}^1EA_{1g}), \quad (16)$$

where $(t_{2g}^6 e_g^2; {}^3A_{2g}) = (t_{2g}^6 e_g^4; {}^1A_{1g}) \times (e_g^2; {}^3A_{2g})$. In other words, the disproportionated system can be viewed as a system of spin-triplet composite hole bosons $(e_g^2; {}^3A_{2g})$ moving in the lattice composed of the electron spin-0 $(t_{2g}^6 e_g^4; {}^1A_{1g})$ centers (see Fig. 1).

In *tetrahedral* or *cubic* crystal field the $3d^9$ system disproportionates as follows:

$$(e_g^4 t_{2g}^5; {}^2T_{2g}) + (e_g^4 t_{2g}^5; {}^2T_{2g}) \rightarrow (e_g^4 t_{2g}^4; {}^3T_{1g}) + (e_g^4 t_{2g}^6; {}^1A_{1g}), \quad (17)$$

where $(e_g^4 t_{2g}^4; {}^3T_{1g}) = (e_g^4 t_{2g}^6; {}^1A_{1g}) \times (t_{2g}^2; {}^3T_{1g})$. In other words, the disproportionated system can be viewed as a system of spin-triplet composite hole bosons $(t_{2g}^2; {}^3T_{1g})$ moving in a lattice composed of the electron spinless $(e_g^4 t_{2g}^6; {}^1A_{1g})$ centers.

3.3. Summary

Let's summarize our findings.

i) The most effective e_g^2 configuration of the local composite boson providing maximal values of the boson transfer integral without strong reduction effects of the electron-lattice coupling is realized only for several *optimal* d^n configurations. These are HS- d^4 , LS- d^7 , d^9 configurations given octahedral crystal field, and d^1 , HS- d^6 configurations given tetrahedral crystal field [42];

ii) All these bare systems are characterized by E-type orbital degeneracy, i.e. these are prone to a strong Jahn-Teller effect. In all the instances the disproportionation reaction lifts the bare orbital degeneracy, that is it has a peculiar "anti-Jahn-Teller" character [43].

iii) All these bare systems are characterized by a strong suppression due to a vibronic reduction of the one-particle (electron or hole) transport, while after disproportionation these are characterized by an effective two-particle (local boson) transport.

iv) Undesirable spin-triplet structure of the local composite bosons appears to be a common feature of all the above mentioned disproportionated systems with a high-symmetry crystal field.

v) At variance with d^1 , d^7 , and d^9 systems the d^4 and d^6 systems reveal unavoidable coexistence of the spin-triplet bosons and a magnetic lattice.

All these results are summarized in Table I where we have added examples of 3d systems with optimal $3d^n$ configurations. The Fig. 3 illustrates the final electronic configurations and two-particle e_g^2 transport for the disproportionation reaction in optimal $d^{4,6,7,9}$ systems.

Our consideration does support and generalize a purely electronic motivation for "negative U " centers which was based upon a stabilization of the electron-rich closed-shell configurations such as ns^2 or nd^{10} through the charge excitation effects or of half-filled configurations such as nd^5 through the exchange-correlation effects (Hund's rule) [8]. The approach does explain the missing oxidation states of ions in s^1 electronic configuration and predict the disproportionational, or charge transfer instability in systems with ions having nominally ns^1 (Hg^+ , Tl^{2+} , Pb^{3+} , Bi^{4+}), d^9 (Cu^{2+}), d^4 (Mn^{3+} , Fe^{4+}), d^6 (Fe^{2+} , Co^{3+}) valence electronic configuration.

Table 1. $3d^n$ JT-systems optimal for the disproportionation driven superconductivity (see text for detail)

| Electron configuration | Symm. | LS/HS | Local boson | Lattice | Parent(bare) compounds | SC |
|--|-------|-------|---|---------|--|-----------------------------------|
| $3d^1(e_g^1):^2E$ Ti^{3+}, V^{4+} | tetra | - | $e_g^{2,3}A_{2g}$ s=1 | S=0 | ? | ? |
| $3d^4(t_{2g}^3e_g^1):^5E$ Mn^{3+}, Fe^{4+} | octa | HS | $e_g^{2,3}A_{2g}$ s=1 | S=3/2 | (Ca,Sr)FeO ₃ RMnO ₃ | NIS, SD T _c , (?) |
| $3d^6(e_g^3t_{2g}^3):^5E$ Fe^{2+}, Co^{3+} | tetra | HS | $e_g^{2,3}A_{2g}$ s=1 | S=5/2 | LaFeAsO,... LiFeAs | NIS, SD T _c ≤ 56 K |
| $3d^7(t_{2g}^6e_g^1):^2E$ Co^{II+}, Ni^{III+} | octa | LS | $e_g^{2,3}A_{2g}$ s=1 | S=0 | RNiO ₃ AgNiO ₂ | ? |
| $3d^9(t_{2g}^6e_g^3):^2E$ Cu^{2+} | octa* | - | $\underline{b}_{1g}^{2,1}A_{1g}$ s=0 | S=0 | La ₂ CuO ₄ ,... YBa ₂ Cu ₄ O ₈ | NIS, SD T _c ≤ 135 K |

In the above we proceed with a conventional approach to the electronic structure of the 3d compounds that implies a predominantly 3d antibonding character of the molecular t_{2g} and e_g orbitals in octahedral MO₆ or tetrahedral MO₄ clusters. Electron and spin density in these clusters is distributed between the 3d ion and ligands that should be taken into account, in particular, when address a so-called "partial" disproportionation such as $Ni^{(3+\delta)+} - Ni^{(3-\delta)+}$ in RNiO₃ [12]. However, upon lowering the crystal field symmetry and anomalous strengthening of the dp -hybridization in the end of the d^n series the situation can change in several important points. Remarkable example is provided by quasi-2D cuprates where we proceed with a strong axial distortion of the CuO₆ octahedra, actually with square CuO₄ plaquettes (D_{4h} point symmetry) as a basic element of the crystal and electronic structure. Single hole $b_{1g}(\propto d_{x^2-y^2})$ -state of Cu²⁺ ion is a typical one for the square-planar coordination of oxygen ions whereas two-hole Cu³⁺ state with the same coordination of oxygen ions seldom exists. Instability of Cu³⁺ ions with 3d⁸, or two-hole $3\bar{d}^2$ configuration is obviously related to a strong inter-electron(hole) repulsion. However, the two-hole state in CuO₄⁵⁻ center to be a cluster analogue of Cu³⁺ ion can be stabilized by a location of the additional hole to low-energy predominantly oxygen O 2p molecular orbitals thus providing a sharp suppression of the inter-electron(hole) repulsion at a relatively small loss in the one-hole energy. In 1988 Zhang and Rice [44] have proposed that the doped hole forms a well isolated local spin and orbital $^1A_{1g}$ singlet state which involves a phase coherent combination of the 2p σ orbitals of the four nearest neighbor oxygens with the same b_{1g} symmetry as for a bare Cu $3d_{x^2-y^2}$ hole. The spin and orbital singlet $\underline{b}_{1g}^2; ^1A_{1g}$, or Zhang-Rice singlet, may be viewed as a local hole composite boson. In other words, the disproportionation $3d^9 + 3d^9 \rightarrow 3d^{10} + 3d^8$ in the tetragonally distorted octahedral $3d^9 = 3\bar{d}^1$ (Cu²⁺) systems gives rise to a system of composite hole S=0 bosons whose spin and orbital structure provides maximal values of the effective

boson transfer integral and minimal boson effective mass, that is optimal conditions for the disproportionation driven high- T_c superconductivity. Such a situation is unlikely realized for the d^1 configuration in a tetrahedral crystal field because of a weak p - d covalency. Thus, our analysis shows that in fact only d^9 system can be a major candidate for maximal T_c 's.

Above we did not concern the energy stability of the final disproportionated "negative- U " state. It should be noted that together with a sizeable recombination energy this implies well isolated ground states of $d^{n\pm 1}$ configurations.

4. Electron-hole Bose liquid with spin-triplet $s = 1$ local composite bosons

Above we have presented a unified approach to the disproportionation phenomenon in different 3d compounds though we did not touch upon such important points as electron and lattice polarization effects, vibronic coupling, and the role played by the spin and orbital degrees of freedom. All these can strongly deform the phase diagram of the 3d compounds from the predictions of the purely charge order parameter model.

Minimal model of the EHBL phase does not imply intervention of the spin degrees of freedom only in quasi-2D cuprates. Indeed, the model considers such a cuprate to be a system of the the spin and orbital singlet $^1A_{1g}$ local S-bosons moving on the lattice formed by hole centers with the well isolated spin and orbital singlet Zhang-Rice $^1A_{1g}$ ground state. For all other "optimal" $3d^n$ systems listed in Table I we arrive at an unavoidable spin-triplet $s = 1$ structure of the composite local bosons moving on the spin (bare octa-HS d^4 and tetra-HS d^6 configurations) or spinless (bare tetra- d^1 and octa-LS d^7 configurations) lattice. In the absence of the external magnetic field the effective Hamiltonian of such an electron-hole Bose liquid takes the form of the Hamiltonian of the quantum lattice Bose gas of the triplet bosons with an exchange coupling [19]:

$$\begin{aligned} \hat{H} = \hat{H}_{QLBG} + \hat{H}_{ex} = & \sum_{i \neq j, m} t_B(ij) \hat{B}_{im}^\dagger \hat{B}_{jm} \\ & + \sum_{i > j} V_{ij} n_i n_j - \mu \sum_i n_i + \sum_{i > j} J_{ij}^{hh} (\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j) \\ & + \sum_{i \neq j} J_{ij}^{hb} (\hat{\mathbf{s}}_i \cdot \hat{\mathbf{S}}_j) + \sum_{i > j} J_{ij}^{bb} (\hat{\mathbf{s}}_i \cdot \hat{\mathbf{s}}_j) + \sum_i J_{ii}^{hb} (\hat{\mathbf{s}}_i \cdot \hat{\mathbf{S}}_i). \end{aligned} \quad (18)$$

Here \hat{B}_{im}^\dagger denotes the $s = 1$ boson creation operator with a spin projection m at the site i ; \hat{B}_{im} is the corresponding annihilation operator. The boson number operator $\hat{n}_{im} = \hat{B}_{im}^\dagger \hat{B}_{im}$ at i -site due to the condition of the on-site infinitely large repulsion $V_{ii} \rightarrow +\infty$ (*hardcore boson*) can take values 0 or 1.

The first term in (18) corresponds to the kinetic energy of the bosons, $t_B(ij)$ is the transfer integral. The second one reflects the effective repulsion ($V_{ij} > 0$) of the bosons located on the neighboring sites. The chemical potential μ is introduced to fix the boson concentration: $n = \frac{1}{N} \sum_i \langle \hat{n}_i \rangle$. For EHBL phase in parent system we arrive at the same number of electron and hole centers, that is to $n = \frac{1}{2}$. The remaining terms in

(18) represent the Heisenberg exchange interaction between the spins of the hole centers (term with J^{hh}), spins of the hole centers and the neighbor boson spins (term with J^{hb}), boson spins (term with J^{bb}), and the very last term in (18) stands for the intra-center Hund exchange between the boson spin and the spin of the hole center. In order to account for the Hund rule one should consider J_{ii}^{hb} to be infinitely large ferromagnetic.

Generally speaking, this model Hamiltonian describes the system that can be considered as a Bose-analogue of the *one orbital* double-exchange model system [45].

More or less simple manifestation of spin degrees of freedom are anticipated for tetra- d^1 and LS-octa- d^7 configurations where we proceed with spin-triplet composite bosons, however, moving on the spinless lattice.

Estimates for different superexchange couplings given the bond geometry typical for manganites such as LaMnO_3 [19] predict antiferromagnetic coupling of the nn hole centers ($J^{hh} > 0$), antiferromagnetic coupling of the two nearest neighbor bosons ($J^{bb} > 0$), and ferromagnetic coupling of the boson and the nearest neighbor hole centers ($J^{hb} < 0$). In other words, we arrive at highly frustrated system of triplet bosons moving in a lattice formed by hole centers when the hole centers tend to order G-type antiferromagnetically, the triplet bosons tend to order ferromagnetically both with respect to its own site and its nearest neighbors. Furthermore, nearest neighboring bosons strongly prefer an antiferromagnetic ordering. Lastly, the boson transport prefers an overall ferromagnetic ordering.

Competition of the Heisenberg exchange and the bosonic double exchange in "optimal" systems such as ferrates $(\text{Ca,Sr})\text{FeO}_3$ or manganites RMnO_3 with bare octa-HS d^4 configurations of the transition metals can be easily demonstrated on an example of the d^5 - d^3 pair, or EH-dimer. The net spin of the EH-dimer is $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$, where \mathbf{S}_1 ($S_1 = 5/2$) and \mathbf{S}_2 ($S_2 = 3/2$) are spins of Fe^{3+} and Fe^{5+} (Mn^{2+} and Mn^{4+}) ions, respectively. In nonrelativistic approximation the spin structure of the EH-dimer will be determined by isotropic Heisenberg exchange coupling

$$V_{ex} = J(\mathbf{S}_1 \cdot \mathbf{S}_2), \quad (19)$$

with J being an exchange integral, and the two-particle charge transfer characterized by a respective transfer integral which depends on spin states as follows:

$$\langle \frac{5}{2} \frac{3}{2}; SM | \hat{H}_B | \frac{3}{2} \frac{5}{2}; SM \rangle = \frac{1}{20} S(S+1) t_B, \quad (20)$$

where t_B is a spinless transfer integral. Making use of this relation we can introduce an effective spin-operator form for the boson transfer as follows:

$$\hat{H}_B^{eff} = \frac{t_B}{20} \left[2(\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2) + S_1(S_1+1) + S_2(S_2+1) \right], \quad (21)$$

which can be a very instructive tool both for qualitative and quantitative analysis of boson transfer effects, in particular, the temperature effects. Both conventional Heisenberg exchange coupling and unconventional two-particle bosonic transfer, or bosonic double exchange can be easily diagonalized in the net spin S representation

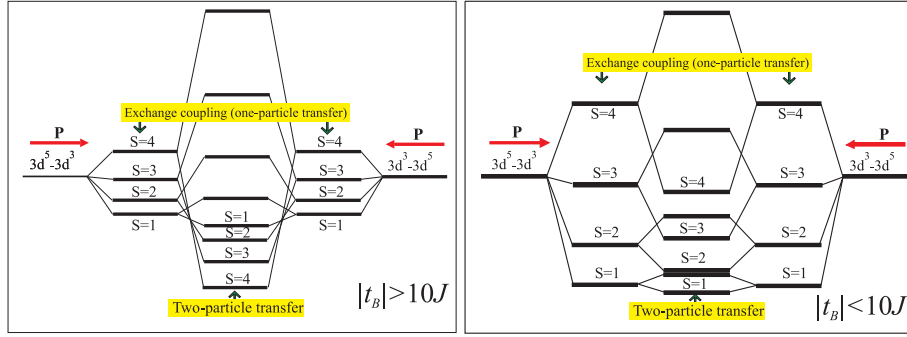


Figure 4. (Color online) Spin structure of the EH-dimer, or self-trapped CT exciton with a step-by-step inclusion of one- and two-particle charge transfer. Arrows point to electric dipole moment for bare site-centered dimer configurations.

so that for the energy we arrive at

$$E_S = \frac{J}{2}[S(S+1) - \frac{25}{2}] \pm \frac{1}{20}S(S+1)t_B, \quad (22)$$

where \pm corresponds to two quantum superpositions $|\pm\rangle$ written in a spin representation as follows

$$|SM\rangle_{\pm} = \frac{1}{\sqrt{2}}(|\frac{5}{2}\frac{3}{2}; SM\rangle \pm |\frac{3}{2}\frac{5}{2}; SM\rangle), \quad (23)$$

with s - and p -type symmetry, respectively. It is worth noting that the bosonic double exchange contribution formally corresponds to a ferromagnetic exchange coupling with $J_B = -\frac{1}{10}|t_B|$.

We see that the cumulative effect of the Heisenberg exchange and the bosonic double exchange results in a stabilization of the $S=4$ high-spin (ferromagnetic) state of the EH-dimer provided $|t_B| > 10J$ and the $S=1$ low-spin (ferrimagnetic) state otherwise (see Fig. 4). As in conventional (one-electron) double exchange model [46] the latter frustration between the Heisenberg exchange and the bosonic double exchange stabilizes a noncollinear ordering in bulk systems.

5. Discussion

Our approach provides a comprehensive understanding of the well established disproportionation in ferrates $(\text{Ca}, \text{Sr})\text{FeO}_3$ and nickellates RNiO_3 with octa-HS d^4 and octa-LS d^7 configurations of the transition metals. It is worth noting that the flexible perovskite structure of both compounds facilitates a screening of the effective correlation parameter U_{dd} . In $(\text{Ca}, \text{Sr})\text{FeO}_3$ the effect is believed to strengthen due to a large enough polarizability of the Ca^{2+} or Sr^{2+} ions while in RNiO_3 we deal with a sizeable reduction of the effective U_{dd} due to a strong Ni-O covalency.

An incommensurate helicoidal spin ordering observed both in CaFeO_3 and SrFeO_3 up to very low temperatures can be explained as a result of a competition between conventional exchange coupling and the bosonic double exchange in EH dimers

$M^\pm \leftrightarrow M^\mp$. Interestingly, the helicoidal spin ordering gives rise to a full (SrFeO₃) or partial (CaFeO₃) suppression of the charge order resulting in a metallic or insulating temperature dependence of the resistivity, respectively [47]. In any case both theoretical and experimental study of the phase diagram for (Ca,Sr)FeO₃ system deserves further work, especially, aimed to a search of a possible superconductivity.

Nominal electronic HS-octa-configuration d^4 of the Fe⁴⁺ ion is analogous to that of Mn³⁺ ion in perovskite (ortho)manganites RMnO₃ that implies similar disproportionation features. Indeed, similarly to ferrates (Ca,Sr)FeO₃ the orthomanganites RMnO₃ reveal a high-temperature metallic phase which may be associated with a fully disproportionated R(Mn²⁺Mn⁴⁺)O₃ phase [18, 19], or EHBL system. Such a conclusion is particularly supported by an anomalously small magnitude of the thermopower. Interestingly that under spin ordering this manganite phase in contrast with the ferrates could become a *ferromagnetic EHBL metal* as bosonic double exchange in manganese EH dimers overcomes the Heisenberg exchange in favour of the ferromagnetic spin state [19]. In other words, in manganites we deal with the high-spin ferromagnetic ground state of the EH dimer (see Fig. 4a), while in ferrates with the low-spin ferrimagnetic one (see Fig. 4b). However, actually upon lowering the temperature one observes a first order phase transition at $T=T_{JT}$ ($T_{JT} \approx 750$ K in LaMnO₃) from the high-temperature fully disproportionated metallic EHBL phase to a low-temperature orbitally ordered insulating phase with a cooperative Jahn-Teller ordering of the occupied e_g -orbitals of the Mn³⁺O₆ octahedra accompanied by A-type antiferromagnetic ordering below T_N ($T_N \approx 140$ K in LaMnO₃) [18, 19]. In other words, the vibronic (Jahn-Teller) coupling in bare (parent) Mn³⁺ phase suppresses the anticipated charge order and does promote a recombination $M^\pm \rightarrow M^0$ transition.

Interestingly that the nonisovalent substitution and/or nonstoichiometry seems to revive the disproportionated phase and such manganites along with a metallic ferromagnetism with a colossal magnetoresistance reveal many properties typical for superconducting materials. These are a steep jump of the specific heat, gap opening in tunneling, and giant proximity effect. Several manganite samples were shown to exhibit a negative diamagnetic susceptibility in a wide temperature range up to room temperature [48]. To explain many experimental manifestations of superconductivity Kim [49] has proposed a superconducting condensation in manganites. In this scenario, colossal magnetoresistance in La_{1-x}Sr_xMnO₃ is naturally explained by the superconducting fluctuations with increasing magnetic fields. This idea is closely related to the observation of anomalous proximity effect between superconducting YBCO and a manganese oxide, La_{1-x}Ca_xMnO₃ or La_{1-x}Sr_xMnO₃ [50], and also the concept of a local superconductivity manifested by doped manganites [51].

A strong evidence of the revived EHBL phase below first order phase transition $M^\pm \rightarrow M^0$ from the high-temperature EHBL phase to low-temperature AFM insulating phase is obtained very recently by Nath *et al.* [52]. The authors observed an electric field driven destabilization of the insulating state in nominally pure LaMnO₃ single crystal with a moderate field which leads to a resistive state transition below 300 K. The effect

has been explained as bias driven percolation type transition between two coexisting phases, where the majority phase is a charge and orbitally ordered polaronic AFM insulating phase and the minority phase is a bad metallic EHBL phase [52].

Very recently distinct signatures of high-temperature disproportionated EHBL phases are revealed also in other manganites, such as $\text{LaMn}_7\text{O}_{12}$ [53] with quadruple perovskite structure and YBaMn_2O_6 [54]. A dramatic suppression of the Curie-Weiss susceptibility in the undistorted phase of $\text{LaMn}_7\text{O}_{12}$ above $T_{JT} \approx 650$ K is explained by a picture of long-lived low-spin $S=1$ EH dimers (see Fig. 4b) formed by the charge transfer between neighboring Mn sites [53]. High-temperature electron spin resonance studies of A-site ordered mixed-valent manganite YBaMn_2O_6 [54] have revealed two puzzles. First, in the metallic high-temperature phase the ESR signal stems only from all Mn^{4+} core spins. Second, the ESR linewidth obeys the Korringa-like linear high-temperature increase over a wide temperature range of 400 K clearly pointing to a truly metallic state. Both findings strongly support our suggestion of the high-temperature EHBL phase of manganites to be a system of spin-triplet composite e_g^2 bosons moving on the lattice of spin-3/2 Mn^{4+} centers. Furthermore, one may speculate that the Korringa-like behavior of the ESR linewidth could be a signature of such a charge-disproportionated picture [54]. Our prediction of the disproportionation driven high- T_c superconductivity in the HS- d^4 octa-systems needs in a more direct validation for the hole doped manganites such as $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$.

High-temperature metallic phase of rare earth nickelates RNiO_3 with LS-octa- d^7 configuration of Ni^{III+} ions resembles that of orthomanganites, however, with a Pauli-like magnetic susceptibility and evidences a full $d-d$ disproportionation. Yet the low-temperature behavior of manganites and nickelates strongly differs. For rhombohedral LaNiO_3 the system remains metallic down to 1.5 K, whereas orthorhombic RNiO_3 ($\text{R} = \text{Pr}, \dots, \text{Lu}$) exhibit a first order phase transition to a charge ordered insulating state upon cooling below T_{CO} spanning from 130 K for Pr to ~ 550 -600 K for heavy rare earths. Both the lighter and heavier orthorhombic RNiO_3 compounds are very similar from the point of view of their local electronic and magnetic CO state despite the strong change of the metal-to-insulator NO-CO transition temperature. All these exhibit clear signatures of the charge disproportionated state with two types of Ni centers corresponding to alternating large NiO_6^{10-} (Ni^{2+} center) and small NiO_6^{8-} (Ni^{4+} center) octahedra strongly differing in magnetic moments ($\sim 2 \mu_B$ and ~ 0 , respectively). Regarding the magnetic order, these nickelates adopt an antiferromagnetic structure defined by the propagation vector $(1/2, 0, 1/2)$ at a transition temperature T_N spanning from 130 K to ~ 200 K. Antiferromagnetic ordering can be explained by a rather strong superexchange nnn (next-nearest neighbor) coupling of magnetic $S=1$ Ni^{2+} centers. Unfortunately, the antiferromagnetism stabilizes the charge order and suppresses the superconductivity.

At variance with the charge transfer unstable perovskites ($(\text{Ca}, \text{Sr})\text{FeO}_3$, RMnO_3 , RNiO_3) the quasi-2D nickelates ANiO_2 ($\text{A} = \text{Ag}, \text{Li}, \text{Na}$) reveal existence of unconventional ground states stabilized by the frustrated triangular lattice geometry from a cooperative JT ordering of Ni^{3+} ions in NaNiO_2 to a *moderately charge ordering*

$3\text{Ni}^{III+} \rightarrow \text{Ni}^{2+} + 2\text{Ni}^{3.5+}$ in antiferromagnetic metal AgNiO_2 [55]. In the case of LiNiO_2 there could be a competition between charge ordering and orbital ordering for the ground state, the nickel valency could be a mixture of 2+, 3+, and 4+ [56].

In all the CT-unstable 3d compounds with *optimal* electron configurations addressed above the JT coupling in nearly octahedral complexes (FeO_6 , MnO_6 , NiO_6) competed with the charge disproportionation and in several compounds this determined the orbitally ordered ground state and the low-temperature phase thus suppressing the anticipated superconductivity. The JT coupling reaches its maximal magnitude in Cu^{2+} octahedral complexes that seemingly should inhibit the disproportionation in Cu^{2+} based cuprates. However, the giant JT distortion stabilizes the CuO_4 plaquette with a $b_{1g} \propto d_{x^2-y^2}$ hole ground state which can be a proper starting orbital for an in-plane hole transfer $\underline{b}_{1g} \rightarrow \underline{b}_{1g}$ in the CuO_2 planes of the quasi-2D cuprates. As a result we arrive at a disproportionation $2\text{CuO}_4^{6-} \rightarrow \text{CuO}_4^{7-} + \text{CuO}_4^{5-}$ with formation of a spin and orbital singlet electron center CuO_4^{7-} (analog of the Cu^+ ion) and a hole center CuO_4^{5-} (analog of the Cu^{3+} ion) in a Zhang-Rice $^1A_{1g}$ ground state. Full disproportionation within a CuO_2 plane results in a system of composite two-electron spin-singlet (S-type) bosons moving on the spin-0 lattice formed by hole CuO_4^{5-} centers. We arrive at a EHBL system which is the most favorable one for the high- T_c superconductivity. A comprehensive argumentation of the disproportionation scenario for quasi-2D cuprates is reported in Ref. [5].

At first sight the situation similar to cuprates can be realized in a hypothetical quasi-2D nickellate with a system of well isolated Ni^{3+}O_2 planes provided a low-spin $t_{2g}^6 e_g$ configuration of the NiO_4^{5-} center with the $b_{1g} \propto d_{x^2-y^2}$ electron ground state and a spin-singlet ZR-type configuration of the e_g^2 -subshell of the electron NiO_4^{6-} center. However, the latter condition seems unlikely to be realized in practice therefore the perspectives of the cuprate-like superconductivity in nickellates look like very illusive [57].

In the above we addressed "optimal" systems with bare octahedral $d^{4,7,9}$ complexes. What about predicted "optimal" d^1 and d^6 systems with tetrahedral local symmetry? At present we have no literature data about such d^1 systems whereas the systems with tetrahedral d^6 , or more precisely, high-spin Fe^{2+} complexes number tens of the so-called iron pnictides ("FePn", where Pn is As or P) and iron chalcogenides ("FeCh", where Ch includes S, Se, and Te) [58]. Actually all these compounds are either superconductors or parent systems which turn into superconducting phase with T_c values up to 56 K under nonisovalent doping and external or "chemical" pressure.

All the families of iron-containing superconductors have two-dimensional planes of FePn_4 or FeCh_4 tetrahedra. The quasi-2D structure makes the iron compounds in common with superconducting cuprates, however, the FePn/Ch superconductors are fundamentally different from the cuprates in several points. First of all it concerns the coexistence of superconductivity with magnetism demonstrated at an unprecedented atomic scale.

Unlike the case of the high- T_c cuprates, electrons in FePn/Ch layers are always itinerant and there is no Mott insulating state in the electronic phase diagram though

most of the FePn/Ch systems start with an AFM order as the parent phase. The magnetic order in FePn/Ch layers is unconventional one, it is most likely a spin-density wave with strongly reduced mean values of a local effective spin.

All the main features of the superconducting and normal state for the FePn/Ch compounds agree with our predictions of the disproportionation within the FePn/Ch layers accompanied by formation of EHBL system with a topological phase separation, e.g. formation of a multi-bubble system. However, in contrast with the spinless scenario for cuprates in the FePn/Ch layers both composite electron e_g^2 bosons and the hole lattice have nonzero spins, $s=1$ and $S=5/2$, respectively. It means that the charge ordered bubbles jointly are magnetic bubbles with a complex nanoscopically inhomogeneous spin structure. Accordingly, the FePn/Ch layers can be considered as a system of the bubble carriers which carry both charge, "local superconductivity", and a spin density. Moreover, the bubble formation is accompanied by strong nanoscale structural distortions which can be detected by pair distribution function analysis [59].

In any case, finding the high- T_c superconductivity in the FePn/Ch compounds with the *tetrahedral* coordination of the iron $\text{Fe}^{2+}(3d^6)$ ions in HS state and its *coexistence* with an unconventional magnetism can be a key argument supporting the disproportionation scenario [60]. Puzzlingly, our model implies the superconducting carriers in FePn/Ch compounds are composed of the e_g rather than t_{2g} electrons as predicted by one-electron band models. Both cuprates and ferro-pnictides/chalcogenides are believed to be "bad" EHBL metals.

6. Conclusion

We analyzed d - d disproportionation phenomena in materials with different 3d ions. We have shown that optimal conditions for the disproportionation driven high- T_c superconductivity are realized only for several d^n configurations. These are HS- d^4 , LS- d^7 , d^9 configurations given octahedral crystal field, and d^1 , HS- d^6 configurations given tetrahedral crystal field. Interestingly, all these bare systems are characterized by E-type orbital degeneracy, i.e. these are prone to a strong Jahn-Teller effect. In all the instances the disproportionation reaction lifts the bare orbital degeneracy, that is it has a peculiar "anti-Jahn-Teller" character. All the optimal systems are characterized by a strong suppression of the one-particle transport, while after disproportionation these are characterized by an effective two-particle transport. Anyhow the optimal disproportionation schemes (see Fig. 3 and Table I) imply a participation of a spin degree of freedom. Proposed superconductivity in the d^4 and d^6 systems at variance with d^1 , d^7 , and d^9 systems is characterized by unavoidable coexistence of the spin-triplet composite bosons and a magnetic lattice. Only quasi-2D cuprates in a "negative- U " regime seem to represent a system of spin-singlet composite bosons moving on the spinless lattice. Their magnetic response could be explained by purely oxygen orbital magnetism if we take into account deviations from the simple Zhang-Rice model [29, 30]. Interestingly, our "spinless" scenario for cuprates clearly opposes to a spin/magnetic mechanism to

be currently a leading contender for the superconducting mechanism in the high T_c cuprates.

We argue that unconventional superconductivity observed in iron-based layered pnictides and chalcogenides with tetrahedrally coordinated Fe^{2+} ions can be a key argument supporting the disproportionation scenario is at work in these compounds. It is worth noting that the potential for high- T_c appears to be the greatest for undistorted FePn_4 tetrahedra [61]. Furthermore, observation of the high- T_c superconductivity in these quasi-2D systems with undesirable spin degrees of freedom both for the composite boson and the lattice gives some hope to finding of superconductivity in artificial 2D superlattices of all the "optimal" configurations.

We did not concern here many important points of the disproportionation scenario and some comparisons with other model approaches, particularly with the bipolaronic theory by Alexandrov [41]. Nevertheless the model approach suggested is believed to provide a conceptual framework for an in-depth understanding on equal footing of physics of very different strongly correlated 3d systems such as cuprates, manganites, nickellates, ferro-pnictides/chalcogenides, and other systems with a charge transfer instability and/or mixed valence. In particular, our paper provides a clear answer to the question, "what is so special about Cu in cuprates or Fe in the Fe-based superconductors?" and why, e.g., BaMn_2As_2 which with respect to many properties is situated between BaFe_2As_2 and the high- T_c cuprates is not a high- T_c superconductor [61].

Acknowledgments

The RFBR grants Nos. 10-02-96032 and 12-02-01039 are acknowledged for providing financial support.

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